ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

REMOVAL OF BORON FROM AQUEOUS SOLUTIONS BY USING TRIS(HYDROXYMETHYL)AMINOMETHANE MODIFIED RESIN

M.Sc. THESIS

Zeynep Ece EREL

Polymer Science& Technology Department

Polymer Science& Technology Programme

JANUARY, 2015

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

REMOVAL OF BORON FROM AQUEOUS SOLUTIONS BY USING TRIS(HYDROXYMETHYL)AMINOMETHANE MODIFIED RESIN

M.Sc. THESIS

Zeynep Ece EREL
(515121018)

Polymer Science& Technology Department

Polymer Science& Technology Programme

Thesis Advisor: Prof. Dr. B. Filiz ŞENKAL

JANUARY, 2015

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

TRİS(HİDROKSİMETİL)AMİNOMETAN İLE MODİFİYE EDİLMİŞ REÇİNENİN SULU ÇÖZELTİLERDEN BOR GİDERİLMESİNDE KULLANILMASI

YÜKSEK LİSANS TEZİ

Zeynep Ece EREL
(515121018)

Polimer Bilim ve Teknolojisi Anabilim Dalı

Polimer Bilim ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. B. Filiz ŞENKAL

OCAK, 2015

Zeynep Ece EREL, a **M.Sc.** student of ITU **Graduate School of.....** student ID **515121018**, successfully defended the **thesis** entitled "…….**THESIS TITLE……..**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. B. Filiz ŞENKAL** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. Name SURNAME** Yıldız Technical University	.....
	Prof. Dr. Name SURNAME Boğaziçi University	.....

Date of Submission :
Date of Defense :

To my family,

FOREWORD

I would like to thank all people who made this work possible. First of all, I would like to thank my thesis advisor, Prof. Dr. Bahire Filiz ŞENKAL, for leading me toward my work, and educating me on polymer chemistry and science.

Moreover, I wish to thank all my lab members for all their help, support and friendship. In particular, Erdem YAVUZ, Gülçin TORUNOĞLU TURAN, Esma AHLATÇIOĞLU, Fatih BİLDİK and Merve HAMAMCI with all of you, it has really been a great pleasure.

I am grateful to my parents Gülsüm and Barbaros EREL, especially I thank to my brother Tolga for supporting me.

Finally, I am really appreciated to Olcay ÖZGÜR for being beside me all the time and also I would like to thank to Elif BAYSAK for her helps during my master education.

January, 2015

Zeynep Ece EREL
(Chemist)

TABLE OF CONTENTS

Page

ABBREVIATIONS

AIBN	**:** Azobisisobutyronitrile
DHPVC	**:** Dehydrochlorinated Poly(vinyl chloride)
DVB	**:** Divinyl Benzene
EDTA	**:** Ethylenediaminetetraacetic Acid
EGDMA	**:** Ethylene Glycol Dimethacrylate
GMA	**:** Glycidyl Methacrylate
MMA	**:** Methyl Methacrylate
PGMA	**:** Poly (glycidyl methacrylate)
RO	**:** Reverse Osmosis
WHO	**:** World Health Organization

LIST OF TABLES

Page

LIST OF FIGURES

Page

REMOVAL OF BORON FROM AQUEOUS SOLUTIONS BY USING TRIS(HYDROXYMETHYL)AMINOMETHANE MODIFIED RESIN

SUMMARY

Boron compounds are used in the glass and ceramic industry to produce borosilicate glass, insulation fiberglass, flame retardant fiberglass, ceramic glazes, neutron absorbers, porcelain enamels, herbicides or fertilizers.

Boron presents in groundwater or surface water in various locations where it occurs mainly in the form of boric acid. Common boron sources in water are urban wastewater containing detergents and cleaning products (washing powders and soaps), industrial effluents from a great number of industrial activities and diverse chemical products used in agriculture.

Boron has the health risks highlighted by the World Health Organization (WHO), on the basis of a study in laboratory animals was found to cause toxicity that consistently targeted the male reproductive tract. Testicular lesions have been observed in rats, mice and dogs given boric acid or borax in food or drinking-water, and a guide level of 2.4 mg L^{-1} has been recommended in drinking water.

Large amounts of boron can affect the central nervous system and the reproductive system in humans. Although small quantities of boron are important for plant growth, high levels are harmful to most species. The maximum recommended boron concentration in irrigation waters varies considerably according to the type of plant: lemon and blackberry plants cannot tolerate boron concentrations greater than 0.5 mg L^{-1} (extremely sensitive plants); orange, peach, cherry, plum, onion, and grape can only tolerate boron concentrations of up to 0.75 mg L^{-1} (very sensitive plants); but sorghum, cotton, celery and asparagus can tolerate boron concentrations of up to 10 mg L^{-1} (very tolerant plants).

There is no easy method available for the removal of boron from water and wastewater. One or more methods may be applied according to boron concentration in the medium. For boron removal, main processes that have been studied are: (1) precipitation–coagulation, (2) reverse osmosis, (3) electrodialysis, (4) solvent extraction, (5) membrane filtration, and (6) adsorption (including ion exchange adsorption). Among these methods, adsorption is a very useful and economical technique at low boron concentration.

In this study, glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EGDMA,10%) were copolymerized to obtain crosslinked poly GMA by using suspension polymerization method. Epoxy content of the resin determined by the pyridine-HCl method was found as 6.15 mmol g^{-1} sorbent. Epoxy group can undergo

ring opening with amines, hyroxyl containing compounds etc. This methodology was applied for crosslinked PGMA.

The resin was reacted with excess of tris(hydroxymethyl)aminomethane to obtain tris(hydroxymethyl)aminomethane modified methacrylate based crosslinked bead polymers.

The resin was characterized by using analytical techniques and FT-IR. Total amine capacity of the resin was found as 2.5 mmol g^{-1} sorbent.

The resin was used to remove boron from water. Therefore, loading capacity of the boron was studied depending on different boron concentration and pH. Hydroxyl functions incorporated into the polymer structure act as chelating agent by forming cyclic boron esters. Boron loading capacity of the sorbent is about 3.2 mmol g^{-1}, in non-buffered conditions. Interestingly, no appreciable change occurs in the pH of the aqueous solutions during boron sorption, and the pH values lie in the 6-6.5 range. pH dependent boron sorption experiments indicated that boron ester formation is stable at pH values above 4.

Batch kinetic sorption experiments were performed with highly diluted boric acid solution (4.9×10^{-3} M) to investigate the efficiency of the resin in the presence of low boron concentrations. The concentration-time plot shows that within about 60 minutes contact time boron concentration falls to zero.

Sorption kinetic models were applied to the resin. The linear form of the equation that describes the adsorption kinetics corresponding to the pseudo second-order model is as follows :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t$$

Where q_e is the amount of boron adsorbed at equilibrium (mg g^{-1}); q_t is amount of boron adsorbed at time t (mg g^{-1}); k_2 is equilibrium rate constant of pseudo second-order sorption (g mg^{-1} min^{-1}). The rate parameters k_2 and q_e can be directly obtained from the intercept and slope of the plot of t/q_t versus t.

If the pseudo-second order kinetics is applicable, the plot gives a linear relationship which allows computation of k_2 value of correlation coefficients showed that the data fitted well to the pseudo-second-order rate kinetic model.

Loaded polymer samples, when treated with 2.5 M HCl become almost boron-free. In this way, 2.9 mmol g^{-1} boric acid is recovered of loaded sample.

TRİS(HYDROKSİMETİL)AMİNOMETAN İLE MODİFİYE EDİLMİŞ REÇİNENİN SULU ÇÖZELTİLERDEN BOR GİDERİLMESİNDE KULLANILMASI

ÖZET

Bor bileşikleri cam ve seramik endüstrisinde borosilikat cam, yalıtkan fiberglas, yanma geciktirici fiberglas, seramik cilası, nötron tutucu, porselen mine üretiminde kullanıldığı gibi tarım ilacı ve gübre yapımında da kullanılmaktadır. Yüksek konsantrasyonda ve ekonomik boyutlardaki bor yatakları, borun oksijen ile bağlanmış bileşikleri olarak daha çok Türkiye ve ABD'nin kurak, volkanik ve hidrotermal aktivitesinin yüksek olduğu bölgelerde bulunmaktadır. Türkiye'de bilinen bor yatakları özellikle Kırka/Eskişehir, Bigadiç/Balıkesir, Kestelek/Bursa ve Emet/Kütahya'da bulunmaktadır.

Türkiye'de rezerv açısından en çok bulunan bor cevherleri tinkal ($Na_2O.2B_2O_3.10H_2O$) ve kolemanit ($2CaO.3B_2O_3.5H_2O$)'tir. Türkiye dünya bor rezervlerinin % 72'sine sahiptir.

Bor yeraltı ve yüzey sularında borik asit şeklinde bulunmaktadır. Deterjan ve temizlik ürünleri içeren şehir atık suları (toz deterjanlar ve sabunlar), sanayi atık suları ve tarımda kullanılan çeşitli kimyasallar sulardaki bor kaynağını oluşturmaktadır. Çevre kirliliğinin önlenmesi adına atık sulardaki borun giderilmesi önem taşır.

Dünya Sağlık Örgütü yapılan bazı çalışmalar ile borun çeşitli zararlarını vurgulamıştır. Hayvanlar ile yapılan laboratuvar çalışmalarında, sıçan, fare ve köpeklerin yiyecek ya da içme sularıyla borik asit ve boraks alması sağlanmıştır. Bu çalışmalarda borun, erkek üreme sistemini hedef alacak şekilde zehirli madde birikimine ve fonksiyon bozukluklarına neden olduğu gözlenmiştir. İçme suyunun içerdiği bor miktarının 2.4 mg L^{-1} olması tavsiye edilmiştir.

Yüksek oranda bor insanlarda merkezi sinir sistemini ve üreme sistemini etkileyebilmektedir. Durum bitkiler açısından değerlendirildiğinde ise çoğu bitki yüksek oranlardaki boru tolere edememektedir. Diğer yandan az miktarda borun bitkilerin büyümesi için gerekli olduğu bilinmektedir. Bitkilerin sulanması için kullanılan suyun içermesi gereken bor konsantrasyonu bitkinin cinsine göre çeşitlilik göstermektedir. Limon ve böğürtlen 0.5 mg L^{-1}'den yüksek bor konsantrasyonunu tolere edemezken (son derece hassas bitkiler); portakal, şeftali, kiraz, erik, soğan ve üzüm en çok 0.75 mg L^{-1} bor konsantrasyonunu tolere edebilmektedir (hassas bitkiler); sorgum, pamuk, kereviz ve kuşkonmaz ise 10 mg L^{-1}'ye kadar olan bor konsantrasyonunu tolere edebilmektedir (dayanıklı bitkiler).

Bitkilerin oluşumunda ve büyümesinde belirli miktarda bor gereklidir. Sulama suyunda gerekli bor limitinin aşılması durumunda bitki ölür. Bu fazla miktar, toprakta birikerek toprağı çoraklaştırabilmekte, hatta bir daha kullanılamaz hale getirebilmektedir. Sulama suyu olarak jeotermal suların kullanımı, yüksek bor içeriği nedeniyle çevreye olumsuz etkide bulunmaktadır. Jeotermal suların yer altı suları ile karışmaları sonucu, tarımsal alanlar etkilenerek bor kirliliği ortaya çıkmaktadır.

Atık sulardan bor giderilebilmesi için ortamın bor derişimine bağlı olarak uygulanabilecek birkaç metod mevcuttur; (1) çöktürme-koagülasyon, (2) ters osmoz, (3) elektrodiyaliz, (4) çözücü ekstraksiyonu, (5) membran teknikleri, (6) adsorpsiyon (iyon değişim adsorpsiyonu dahil). Düşük bor konsantrasyonlarında çalışmak için seçilebilecek en ugun ve ekonomik seçenek adsorpsiyon yöntemidir.

Bor sulu çözeltilerinde Lewis asidi özelliği gösterir. Borun adsorpsiyon yöntemi ile sulu çözeltilerden giderilmesini sağlayan kimyasal özelliği ise hidroksil gruplarıyla bor esteri oluşturmasıdır. Birbirine komşu ve cis- konumdaki hidroksil grupları ile borun, bor esteri oluşturduğu bilinmektedir.

Bu çalışmada, glisidil metakrilat (GMA) ve etilen glikol dimetakrilat (EGDMA, % 10) süspansiyon polimerizasyonu yöntemi ile kopolimerleştirilerek çaprazbağlı poli(glisidil metakrilat) (PGMA) bazlı reçine elde edilmiştir. Çaprazbağlı PGMA elde edildikten sonra reçinenin içerdiği epoksi miktarını tespit etmek için pridin-HCl yöntemi uygulanmıştır. Yapılan deneylerin sonucunda epoksi miktarı 6.15 mmol g^{-1} adsorbant olarak bulunmuştur.

Epoksi gruplarının aminler ile halka açılma reaksiyonu verdiği bilinmektedir. Çaprazbağlı PGMA'ya bu metot uygulanmıştır. Reçine yeterli miktarda tris(hidroksimetil)aminometan ile etkileştirilerek, tris(hidroksimetil)aminometan ile modifiye edilmiş metakrilat bazlı çaprazbağlı polimer kürecikleri elde edilmiştir. Analitik yöntemler ve FT-IR kullanılarak reçinenin karakterizasyonu yapılmıştır. Yapılan analitik ölçümlerle reçinenin içerdiği amin miktarı 2.5 mmol g^{-1} olarak bulunmuştur.

Reçine sudan bor giderilmesinde kullanılmıştır. Bu amaçla önce farklı bor konsantrasyonlarında, daha sonra ise farklı pH değerlerinde denemeler yapılarak reçinenin bor tutma kapasitesi ölçülmüştür. Polimer yapısı üzerindeki hidroksil grupları şelat yapıcı ajan gibi davranarak halkalı bor esteri yapısı oluşturmuştur. Tampon çözelti kullanılmadan yapılan ölçümlerde adsorbantın bor tutma kapasitesi 3.2 mmol g^{-1} olarak tespit edilmiştir. Bor adsorpsiyonu esnasında sulu çözeltinin pH'si 6-6.5 arasında kalarak belirgin bir değişiklik göstermemiştir. Farklı pH' lardaki denemeler ise bor adsorpsiyonunun pH 4' ün üzerinde daha kararlı olduğunu göstermiştir.

Bütün adsorpsiyon kinetiği deneyleri seyreltik borik asit çözeltisi ($4.9x10^{-3}$ M) kullanılarak yapılmıştır. Düşük bor konsantrasyonunda reçinenin etkinliği incelenmiştir. Konsantrasyon- zaman grafiği, 60 dakika içerisinde ortamdaki bor derişiminin sıfıra yaklaştığını göstermiştir. Yapılan çalışma ile seyreltik ortamda reçinenin etkin bir şekilde adsorpsiyon yaptığı belirlenmiştir.

Reçineye adsorpsiyon kinetiği modelleri uygulanmıştır. İkinci mertebe kinetik modelinin eşitliği aşağıda belirtildiği gibidir:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t$$

q_e, denge anında adsorplanmış bor miktarını (mg g^{-1}); q_t, t anında adsorplanmış olan bor miktarını (mg g^{-1}), k_2 ise ikinci mertebe adsorpsiyon kinetiği denge sabitini (g mg^{-1} min^{-1}) ifade etmektedir. t/q_t' ye karşılık t grafiğinin çizilmesi ile elde edilen

eğim ve kayım değerleri kullanılarak k_2 ve q_e değerleri hesaplanmıştır. Ortaya çıkan lineer grafik ve buna bağlı olarak hesaplanan korelasyon katsayısı, yalancı ikinci mertebeye uyan bir adsorpsiyon kinetik modeli olduğunu göstermiştir. Buna ek olarak q_e ve q_{eq} değerleri karşılaştırıldığında da adsorpsiyon modelinin yalancı ikinci mertebeye uyumlu olduğu gözlenmiştir.Polimerin bor adsorpsiyon kinetiğinin ikinci mertebe kinetik modeline uygun olduğu bulunmuştur.

Bor yüklü reçine örnekleri 2.5 M HCl ile etkileştirilip reçinenin rejenerasyonu sağlanmıştır. Bu şekilde reçineden 2.9 mmol g^{-1} borik asit desorbe olmuştur.

Yapılan çalışmalar sonucunda sentezlenen reçinenin çeşitli bor konsantrasyonlarında etkili bir şekilde bor adsorplayabildiği gözlenmiştir. Reçine HCl ile etkileştirildiğinde, adsorpladığı bor miktarının tamamına yakınını desorbe edebilmiştir. Böylelikle reçinenin rejenerasyonu sağlanmıştır.

1. INTRODUCTION

Boron and its compounds are widely used in a variety of industries, such as for control rods in the nuclear energy industry, as a buffer component for the deposition of nickel in the electroplating industry, as a significant component of steel and glass, as fire retardants, fertilizers, herbicides and insecticides laundry additives. Boron is widely distributed in nature and is naturally found in minerals, rocks, coal, plants and natural waters.

Boron and its compounds are a wide spread environmental problem, since even a few ppm present in irrigation water can cause stunting of plant growth. For some crops, 1 to 2 ppm may be toxic. Boron also has virulence for reproduction and causes disease in the nervous system of animals.

Numerous works have been done for boron from wastewaters. Amberlite IRA 743, a boron specific resin, was used in boron removal from drinking waters, boron containing wastewaters or geothermal waste waters. N-methyl-D-glucamine-type chelating resins such as Diaion CRB 01, Diaion CRB 02, Purolite S 108 and Purolite S 108 were used in boron removal from wastewaters of geothermal plants .

Vicinal-diol functions polymers such as sorbitol and mannitol are able to bind boric acid specifically by forming stable boron esters even in aqueous solutions.

Epoxy groups can undergo ring opening with various compounds possessing hydroxyl, amine, or activated methylene groups.

In this study, this analogy has been extended to prepare tris(hydroxymethyl)aminomethane modified methacrylate based crosslinked bead polymers. This resin was used for removal of boron from water.

2. THEORETICAL PART

2.1 Polymerization Techniques

Free radical polymerizations are usually performed using one of four different methods: bulk polymerization, solution polymerization, emulsion polymerization and suspension polymerization.

2.1.1 Bulk polymerization

Bulk polymerization is the simplest technique to obtain the less contaminated product. For radical chain polymerization in bulk,undiluted monomer and initiator are used. The initiator decomposes and almost reaches vanishing concentration at the end of the polymerization so optically clear polymers can be obtained. Bulk polymerization is difficult to control because of its highly exothermic nature and the tendency toward the gel effect and also contiuous stirring systems are required. Over heating may also lead to the phenomenon of autoacceleration or gel effect. Because of the local hot spots, discoloration, thermal degradation, branching, development of chain unsaturation or even cross-linking may occur.

There are two approaches to avoid heat and the viscosity problem:

(i) by carrying out the polymerization to low conversions with seperation and recycling of unreacted monomer; and

(ii) by accomplishing the polymerization in stages.

Bulk polymerization is most likely used for step polymerization rather than chain polymerization. However, it is used in the polyethylene, polystyrene and polymethyl methacrylate synthesis [1].

2.1.2 Solution polymerization

This method enables good control of temperature while the solvent is acting as a diluent and reduces viscosity of the system. Solution polymerization, however,

requires flammable or hazardous solvent and removal or recovery of the solvent at the end of the process to isolate the polymer. The solvent may also affect the purification of the product. If the solvent to be used is not chosen with appropriate consideration, chain transfer to solvent may also become a problem.

Solution polymerization is, however, sometimes advantageous to utilize the polymer product in solution, as with coatings and paints [1].

2.1.3 Suspension polymerization

This is a popular method that combines the possitive effects of both the bulk and solution polymerization techniques. Water is commanly used as suspension medium for all water insoluable monomers. Mostly polystyrene, polymethyl methacrylate, polyvinyl chloride, and polyvinyl acetate are obtained via suspension polymerization [1].

In suspension polymerization some additives (stabilizers) are needed, enabling the dispersion of monomer droplets and preventing coagulation [2]. Water soluable polymers at low concentrations such as carboxymethyl cellulose or methyl cellulose, poly(vinyl alcohol), gelatin are used as stabilizers. By forming a thin layer on the monomer-polymer droplets, they stabilize the polymerization and increase the medium viscosity. Bentonite, kaolin, megnesium silicate, and aluminium hydroxide are common water insoluable inorganic compounds that are used to avoid agglomeration of the monomer droplets. Monomer soluble initiators such as organic peroxides, hydroperoxides or azo compounds are prefered instead of oil-soluble initiators.

As it is showed in Figure 2.1, the reaction occurs in the monomer droplets in which the initiator is dissolved. Each monomer droplets act as miniature bulk polymerization system. The product is obtained as “pearls” that are handy for further processes such as functionalization.The size of the droplets varies from 0.1-5 μm in diameter. Final product may contain trace amount of initiator and stabilizers.Efficient drying and elimination of dispersing additives are crucial [2].

As compared to bulk polymerization, heat and viscosity control is easier in the suspension polymerization because the water absorbs heat and provides good control of temperature [1].

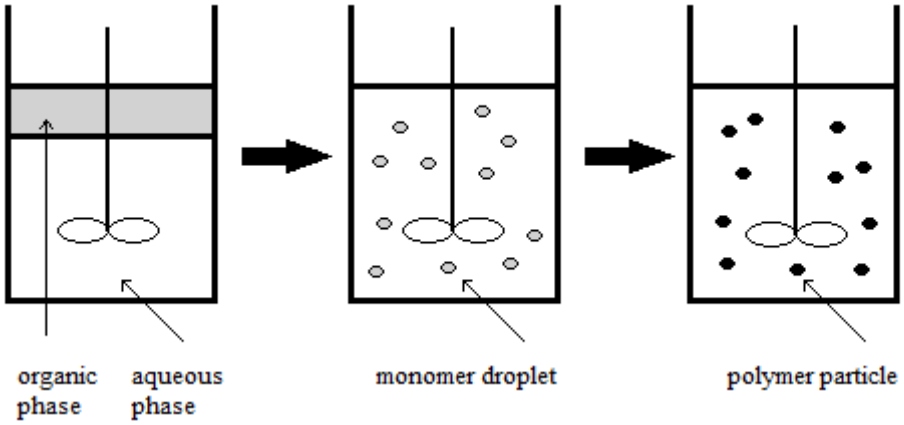

Figure 2.1 : Suspension polymerization.

2.1.4 Emulsion polymerization

In general, an emulsion polymerization system would consist of the following ingredients: monomer(s), dispersing medium, emulsifying agent, water-soluble initiator, and, possibly, a transfer agent. Water is used as the dispersing medium and also acts as a heat transfer medium. Monomers such as styrene, acrylates, methacrylates, vinyl chloride, butadiene show only a slight solubility in water and are able to polymeriza via emulsion polymerization [1].

The initiator is water soluble and the monomer molecules diffuse into the hydrophobic interior of the micelles while water is attracted to the hydrophilic exterior zone. Thus, the micelles serve as the core of growing polymer particles.

Emulsion polymerization provides improved thermal control, results in a higher rate of production.This method is preferred to obtain higher molecular weights and a narrow molecular weight distribution [2]. The product of an emulsion polymerization, referred to as a latex, can be used directly without further separations.

2.2 Functional Polymers

Functional polymers are macromolecules to which chemically bound functional groups are attached which can be utilised as reagents, catalysts, protecting groups, etc. Most functional polymers are based on simple linear backbones. These can be chain-end (telechelic), in-chain, block, crosslinked or graft structures. However, there has also been interest in functional polymers with special topologies or

architectures.[3] These include 3-dimensional polymers, such as stars, hyperbranched polymers, [4, 5] or dendrimers .

The polymer properties can be modified either by chemical reactions on pendant groups or by changing the physical nature of the polymers, such as their physical form, porosity and solvation behaviour. Chemical reaction for the introduction of functional groups in polymers and the functional group conversion in polymers are dependent on the nature of the polymer backbone, nature and degree of crosslinking, pore-volume and pore-size of the polymer particles, separation of the functional groups from the polymer backbone, hydrophobic-hydrophilic balance, solvation and swelling behaviour. The overall three-dimensional structure, stereochemistry of the polymer backbone and the variables of polymerization conditions dictate the nature and reactivity of attached functional groups.

The use of crosslinked polymers in chemical applications is associated with some advantages, such as insolublity in solvents, preparation in the form of spherical beads, seperation. filtration and washing with common solvents, besides, polymer beads with very low degrees of crosslinking swell extensively, exposing their inner reactive groups to the soluble reagents. Also,more highly crosslinked resins may be prepared with very porose structures which allow solvents and reagents to penetrate inside of the beads to contact reactive groups.

2.3 Boron Chemistry

Boron is a omnipresent element in rocks, soil and water, and although it is widely distributed in nature, it occurs in nature only in low and very low concentrations [6].It is known as the average content of boron in the earth crust is 10 mg/L [7]. In soils its average concentration is in the range of 10–20 mg/L. There are large areas of the world suffering for deficiency of this element. Seawater contains an average of 4.6 mg/L boron with variation of concentration from 0.5 to 9.6 mg/L. The concentration of boron in fresh water is usually from less than 0.01 mg/L to 1.5 mg/L and increases significantly in areas where soils are boron enriched — the western part of the U.S., and a ground stretching from the Mediterranean Sea to Kazakhstan [8]. In nature, boron is found as various forms of complex compounds combining with oxygen and other elements. It is found mostly in the form of minerals with different amounts of calcium, sodium or magnesium. The most popular boron forms

are: borax, tincal, colemanite, ulexite and kernite [9]. Boron can occur in nature in the form of: undissociated orthoboric acid, partially dissociated borate anions in the form of polyborates, complexes of transition metals and fluoroborate complexes [10].

Boron appears in the form of boric acid, $B(OH)_3$, in aqueous solutions and it behaves as a very weak Lewis acid. It dissociates as shown in the Eq. **2.1**;

$$B(OH)_3 + H_2O \leftrightharpoons B(OH)_4^- + H^+ \quad \textbf{(2.1)}$$

As can be seen in Equation 1, boric acid does not dissociate in solution but ionizes to form the hydroxyborate ion (tetraborate) in a reaction with a pKa of 9.24. When hydroxyborate and boric acid exist in an aqueous solution, polymerization with the additional formation of water can occur [11].

H_3BO_3 and $B(OH)_4^-$ combine with some organic polyhydroxy compounds which form stable complexes. Examples of such compounds are glycerol and mannitol. The complexes enhance the acid strength of H_3BO_3 remarkably.

2.4 Effect of Boron on Plants

Boron is a micronutrient essential for growing fruits and vegetables [12]. This is the element of special attention as its deficiency and excess are harmful for many plants, and the gap between both these levels is very narrow [8, 13, 14]. Boron plays an important role in the normal growth and functioning of plants [14, 15] while its deficiency inhibits growth of meristematic tissue,disrupts normal cell formation and delays enzymatic reactions. The visible effects can be seen in the interruption of root and leaf growth, leaf thickening, bark cracking, poor budding, excessive branching and reduction of germination [14, 16, 17].

When boron amount is higher than required, there are signs of toxic effects: yellow tips of leaves, defoliation, spots on fruits, decay and fall of unripe fruit [12- 14, 16, 18, 19]. In agricultural production, boron toxicity is more difficult to manage than boron deficiency which can be avoided by proper fertilization [15]. Different plants can tolerate boron on a different level. Some plants are more and some less sensitive to the excess of boron compounds [18].

2.5 Effect of Boron on Animals and Humans

According to the medical and biological research, boron compounds are among the second group of toxic substances [12]. Since 1981 there have been many studies on the different species of animals that showed the effect of boron deficiency on the composition and functioning of many parts of an animal's body [9]. This element has a positive effect on the metabolism of several other nutrients such as calcium, copper or nitrogen [20]. It was noted that boron deficiency reduced absorption of calcium, magnesium and phosphorus [9]. Boron is also an important element in the humans' diet, but its function is not so unequivocal as for plants [9] and its essence of action is not fully understood. The mammalian organisms need boron only in very small amounts. World Health Organization has defined 1–13 mg/day dose of boron as safe and adequate for a healthy individual [21].

Long-term consumption of water and food with increased boron content results in creation of problems with cardiovascular, coronary, nervous and reproductive systems. Moreover, it causes changes in blood composition, neurological effects, physical disorders and intellectual development of children [21,22]. Boron is found naturally in fresh and dried fruits, as well as in vegetables, nuts and in wine [21]. Mammalians do not display any effect on boron deficiency and the organisms need only the amounts that come from food [22].

2.6 Boron Removal Technologies

The major methods for boron removal from water are described below.

For boron removal, main processes that have been studied are: (1) precipitation–coagulation, (2) reverse osmosis, (3) electro dialysis, (4) solvent extraction, (5) membrane filtration, and (6) adsorption (including ion exchange adsorption) [23,24]. Among these methods, adsorption is a very useful and economical technique at low boron concentration [23,25].

2.6.1 Reverse osmosis

Reverse osmosis is a widely utilised membrane technology for seawater desalination. The basic concept reverse osmosis is to utilize a semi-permeable membrane where most of the dissolved species are rejected while water permeates it. Normally, water

spontaneously diffuses through a semi-permeable membrane from a dilute solution to a concentrated solution. However, the reverse process is realised by applying external pressure enough to overcome the osmotic pressure on seawater. This phenomenon is the basis of seawater desalination and water treatment by RO.

However, reverse osmosis technologies are not able sometimes to reduce the boron content below permissible level. So, it is necessary to introduce an additional process to the boron removal line. So as to remove residual boric acid, pH has to be raised to the value of 10-11 in most of the membrane processes [26]. At pH values above 7-8, boric acid transforms to borates that are further processed.

2.6.2 Solvent extraction

Other extensively reported techniques for removing boron from a solution, that is evaporation-crystallization and solvent extraction processes, were declared to be efficient in high concentration streams and to be utilized more for the production of boric acid rather than its removal from aqueous streams [27-29]. One of the drawbacks of the extraction processes is the requirement of specially synthesized extractants, which are expensive and need multistage systems [30-32]. The problem for adsorption process is also present for the process of boron extraction with some water-insoluble diols, that the process requires large number of stages for an adequate removal. Solvent losses throughout the extraction processes are also an additional disadvantage [33].

2.6.3 Precipitation-coagulation

The other alternative for boron removal which is flocculation-precipitation process requires physical-chemical treatments. Those treatments were mentioned not to be economical because of the significant amount of use of expensive flocculants.

2.6.4 Adsorption

The application of chelating resin, seems to be one of the most effective methods among the technology commonly used for the removal of boron from aqueous solutions [34]. The chelating resins containing ligands having three or more hydroxyl groups, located in the cis position, show a high selectivity to boron, conversely these

groups are not reactive to ordinary metals and other elements. Molecules of polyoxide compounds tend to bond through the formation of boric acid esters of boron or borate anion complexes with a proton as a counterion [8, 12, 35, 36].

2.6.4.1 Mechanism of boron removal

The principle of boron selective resins is the use of complexation reactions. Boric acid reacts with compounds possessing multi hydroxyl groups (polyols) to form a variety of borate esters, in accordance with Eq. **(2.2)** where R is a hydrocarbon group. The esters formed rapidly dissociate releasing protons. Thus, the amount of acidification produced upon the addition of the polyols is proportional to the extent of ester formation, which is used for monitoring the reaction [37].

$$B(OH)_3 + 3ROH \leftrightharpoons B(OR)_3 + 3H_2O \qquad \textbf{(2.2)}$$

The stability of the borate complex formed strongly depends on the type of diol used. According to Power and Woods [36], a strong complex is formed when the diol used involves the hydroxyl groups oriented in such a way that they accurately match the structural parameters required by tetrahedrally coordinated boron. For example, a stable complex is formed by the reaction of boron with compounds possessing cis-diol system such as D-mannitol, D-sorbitol, and D-ribose [38]. The most commonly used boron specific resin is Amberlite IRA-743 with sorbitol functional groups and this resin was stated to be forming complexes with boron and it is highly selective [33, 39, 40].

In this case, stable borate complex, cis-diol monoborate ester or bis-diol borate complex is formed, which are shown in Figure 2.2.

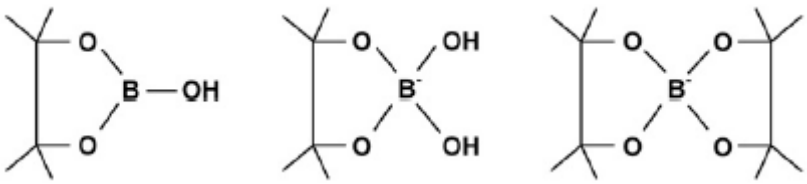

Figure 2.2 : Schematic drawings of the neutral cis-diol monoborate ester (left), the monoborate complex (middle) and the bis(diol) borate complex (right).

The functional group has a tertiary amine end and a polyol end, which is shown in Figure 2.3.

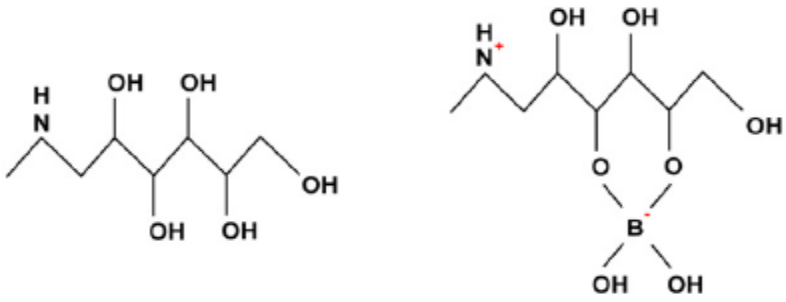

Figure 2.3 : Structural formula of N-methyl-D-glucamine (left) and monoborate complex (right).

The role of the tertiary amine in the functional group is to neutralise the proton brought by the formation of tetra borate complex. Amine protonation is critical to prevent the decrease of pH by proton released from the dissociation of borate esters. As far as hydroxyl groups are concerned, there are 5 hydroxyl groups in N-methyl-D-glucamine. This allows the formation of a strong complex with boron and improves the possibility of complexation by offering several sites for boron.

Sorption with selective and regenerable resins has emerged as an efficient and cost-effective process for extracting boron from aqueous solutions.

Terpolymers of glycidyl methacrylate (GMA)–methyl methacrylate (MMA)–divinyl benzene (DVB) was prepared and modified with N-methyl-D-glucamine. The resin was used for removal of boron [41].

Polymer supported core-shell type iminodipropylene glycol functions have been shown to Dehydrochlorinated poly (vinyl chloride) (DHPVC) polymeric sorbent was synthesized and graft copolymerization of glycidyl methacrylate(GMA) onto DHPVC was carried out using ATRP method. The epoxy rings in grafted PGMA reacted with excess of ethylenediamine to give an amine containing sorbent. Reaction of the latter with glycidol gives corresponding sorbent with iminopropylene glycol functions. be efficient in chelation with boric acid and can be used for removal of boric acid at ppm levels [42].

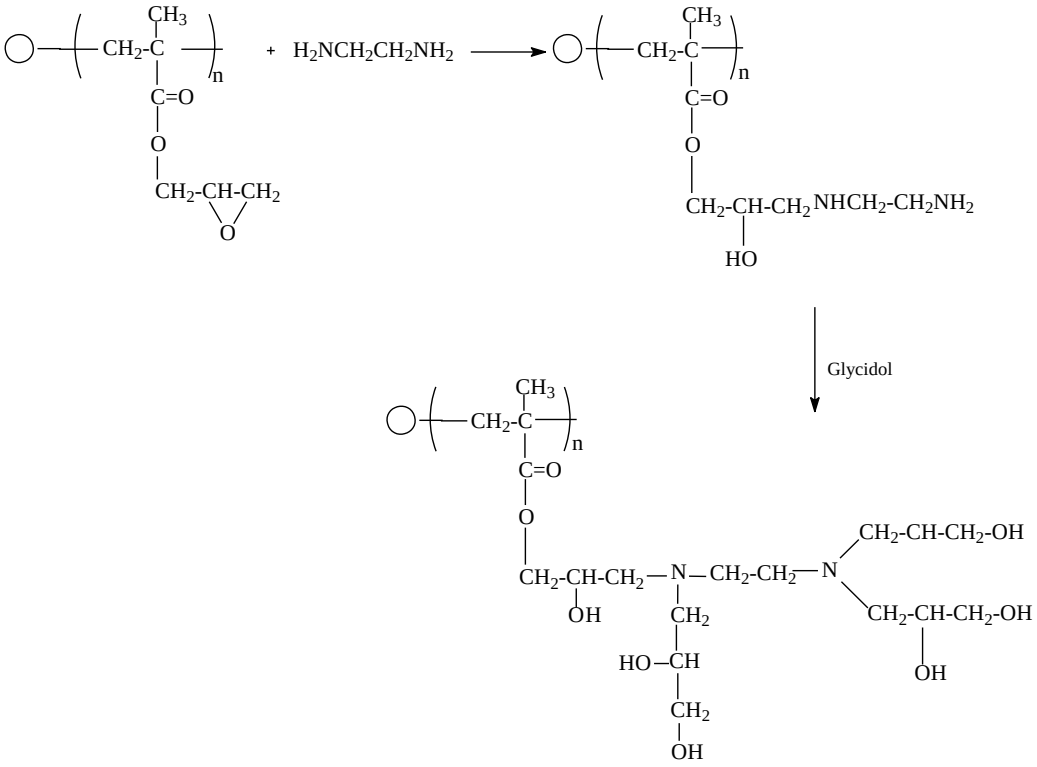

Figure 2.4 : Preparation of iminopropylene glycole modified sorbent.

3. EXPERIMENTAL

3.1 Materials and Methods

All chemicals used were analytical grade: Glycidyl methacrylate (GMA) (Aldrich), Ethylene glycol dimethacrylate (EGDMA)(Aldrich), tris(hydroxymethyl) aminomethane (Aldrich), Boric acid (E-Merck) and all the other chemicals and solvents utilized were analytical grade commercial products.

UV-Vis Spectrophotometer (Perkin-Elmer Lamda 25), FT-IR Spectrophotometer (Nicholet) and orbital shaker were used.

3.2 Preparation of GMA-EGDMA Copolymer Beads

Poly(vinyl pyrrolidone) (1 g) was dissolved in 115 mL of water. Then the solution was transferred to a 1-L three-necked flask equipped with a nitrogen inlet, mechanical stirrer, and reflux condenser. A mixture of 20 mL (0.147 mol) of GMA, 3.1 mL (16.3 mmol) of EGDMA, and 0.5 g (3.05×10^{-3} mol) of azobisisobutyronitrile (AIBN) in 23 mL of toluene was added to the flask under a nitrogen stream. The mixture was heated to 70°C and stirred continuously (ca. 400 rpm) in a nitrogen atmosphere for 5 h. The bead product was filtered and washed consecutively with excess water, acetone, and methanol. Then the beads were dried in vacuum at room temperature for 24 h, and the yield was 23.8 g.

3.3 Determination of Epoxy Content

The epoxy content of the polymer beads was determined by a pyridine-HCl method [43]. 1.6 mL of concentrated HC1 solution (37 %) was added to pyridine and diluted to 100 mL. 10 mL of this solution was boiled with 0.10 g of polymer for 1 h. The mixture was cooled to room temperature and filtered then 2 ml of the filtered solution were titrated with 0.1 M NaOH solution. The epoxy content of the resin was calculated with respect to the differences between the NaOH consumptions in

titrations. Titration of the filtrated pyridine-HCl solution with NaOH (0.052 M) gave 6.15 mmol.g^{-1} epoxy content.

3.4 Modification of GMA-EGDMA Copolymer by Tris(hydroxymethyl) Aminomethane

5 g of GMA-EGDMA copolymer beads were added portion wise to the stirred solution of 14 g of tris(hydroxymethyl) aminomethane in 50 mL of N-methyl pyrrolidione at room temperature. The mixture was placed on a continuous shaker and shaken for 24h at room temperature and the reaction content was heated for 2h at 80 ^{0}C.

The reaction content was filtered and washed with excess of water and 150 ml of methanol respectively. The filtered product was dried under vacuum at room temperature for 24h. The dry product weighted 7.59 g.

3.5 Determination of Amine Content

For determination of the amine content, 0.1 g of the polymer sample was soaked in a solution of 0.1 M HCl (10 ml) and the mixture was shaken by a continuous shaker for 24 h at room temperature. The mixture was filtered and 2 mL of filtrate was taken and the acid content of the solution was determined by titration with 0.05 M NaOH solution in the presence of phenolphthalein color indicator. A total amine content of the resin was calculated as 2.50 mmol g^{-1} sorbent.

3.6 Boron Loading Capacity of Sorbent

The capacity of the sorbent was determined by batch method as follows:

0.1 g of the sorbent sample was mixed with 10 mL of H_3BO_3 solution (0.49 M) and was stirred for 24 h at room temperature. For the determination of residual boric acid content of the filtrate, 2 ml of the filtrate was mixed with 10 ml of 0.50 M D-sorbitol solution and titrated with 0.05 M NaOH solution in the presence of phenolphthalein as a color indicator, as described in the literature [44]. The capacity of the sorbent was calculated as 3.2 mmol g^{-1} of the sorbent sample. Boron sorption capacities of the resin was studied by using different boron concentration. Also, pH depending

sorption experiments were performed in the presence of buffer solutions by using the carminic acid method [45].

3.7 Boron Sorption Kinetics of Sorbent

Batch kinetic experiment was carried out as follows:

0.1 g of the sorbent was soaked into 5 ml of water and left for 2 h. Then, 90 ml of H_3BO_3 solution (4.9×10^{-3} M) was added to the wetted sorbents at room temperature. The mixture was stirred with a magnetic stirring bar. 3 mL of aliquots was taken and transferred to sample-bottles at appropriate time intervals using a filter paper. The carminic acid method was used to determine boron content of the solution (λ=585 nm).

3.8 Desorption of the Boron from Loaded Sorbent

Acid leaching method was used for desorption of the boron as follows:

Loaded sorbent sample (0.1 g) was left in contact with 3 mL of water for 4 h. 8 mL of 2.5 M HCl solution was added and stirred at room temperature for 24 h. After filtrating, 2 mL of the filtrate was titrated with 0.05 M KOH solution in the presence of phenolphthalein indicator. At the end of the neutralization of the excess HCl, 10 ml of 0.5 M D-sorbitol solution was added to the mixture. Additional KOH solution reveals a 2.90 mmol of desorbed boron per gram of loaded sample.

4. RESULTS AND DISCUSSION

In this study, crosslinked poly (glycidyl methacrylate) resin was reacted with tris(hydroxymethyl) aminomethane to obtain tetrahydroxymethyl amino methane function (Figure 4.1).

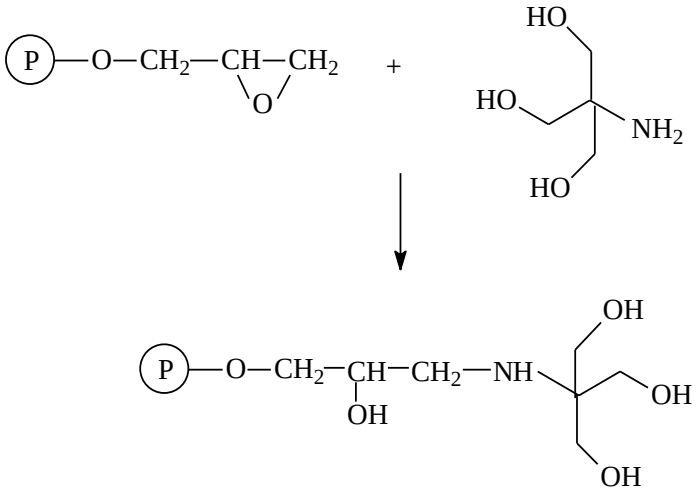

Figure 4.1 : Synthesis of polymeric sorbent.

Epoxy content of the resin determined by the pyridine–HCl method was found as 6.15 mmol.g^{-1} sorbent. The sorbents were characterized by using FT-IR spectrum. FT-IR spectra of the PGMA beads in Figure 4.2 (a) represent strong C=O stretching vibrations at 1726 cm^{-1}. Also, symmetric and asymmetric vibrations of the epoxy ring are observed at 1247 and 947 cm^{-1}, respectively.

The reaction of epoxy rings with excess of tris(hydroxymethyl) aminomethane gives amine containing resin with 2.5 mmol.g^{-1} amine functions.

Figure 4.2 (b) shows the FT-IR spectrum of the resulting tris(hydroxymethyl) amino methane modified sorbent. The broad band in the 3367 cm^{-1} indicates OH stretching vibrations in the sorbent.

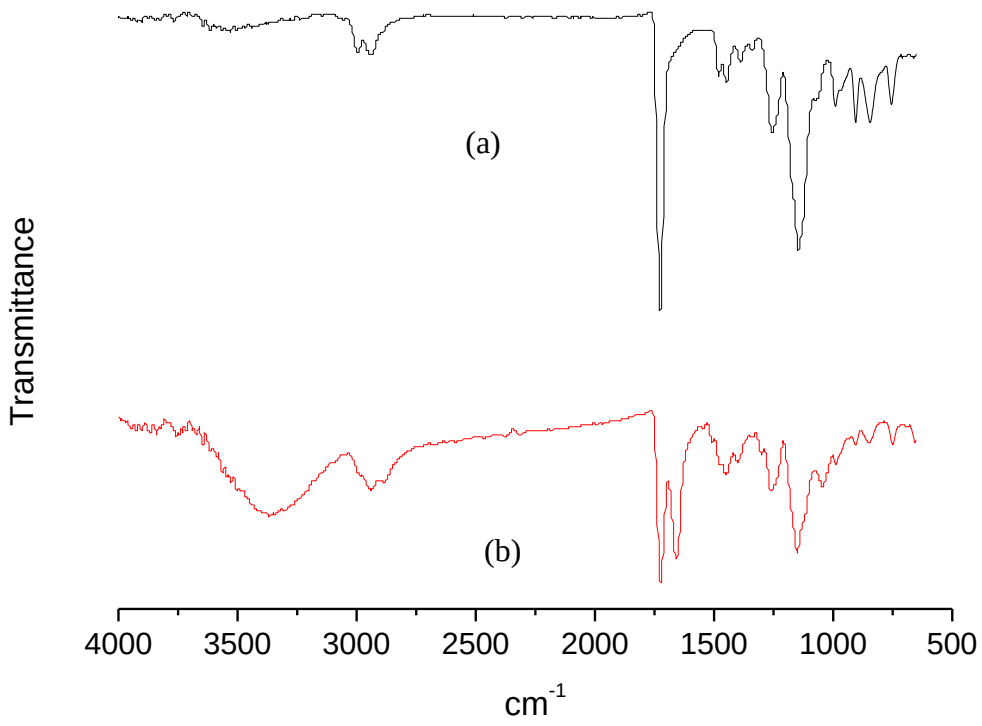

Figure 4.2 : FT-IR spectrum of (a) PGMA resin (b) tris(hydroxymethyl) aminomethane modified resin.

4.1 Boron Uptake

Batch extraction experiments were investigated depending on different boron concentration and pH. Hydroxyl functions incorporated into the polymer structure act as chelating agent by forming cyclic boron esters. Boron loading capacity of the sorbent is about 3.2 mmol g^{-1}, in non-buffered conditions. Interestingly, no appreciable change occurs in the pH of the aqueous solutions during boron sorption, and the pH values lie in the 6-6.5 range.

pH dependent boron sorption experiments (Table 4.1) indicated that boron ester formation is stable at pH values above 4 [46].

Table 4.1 Maximum sorption capacities of the resin depending on pH and at non-buffered conditions.

$[H_3BO_3]$, M	pH	Capacity (mmol g^{-1})
0.490	4.0	3.00
0.490	8.0	2.73
0.490	Non-buffered (pH 6–6.5)	3.20
0.294	Non-buffered (pH 6–6.5)	2.90
0.196	Non-buffered (pH 6–6.5)	2.12
0.098	Non-buffered (pH 6–6.5)	1.63

4.2 Boron Adsorption Kinetics of Resin

Batch kinetic sorption experiments were performed with highly diluted boric acid solution ($4.9x10^{-3}$ M) to investigate the efficiency of the resin in the presence of low boron concentrations. The concentration–time plot (Figure 4.3) shows that within about 60 minutes contact time boron concentration falls to zero.

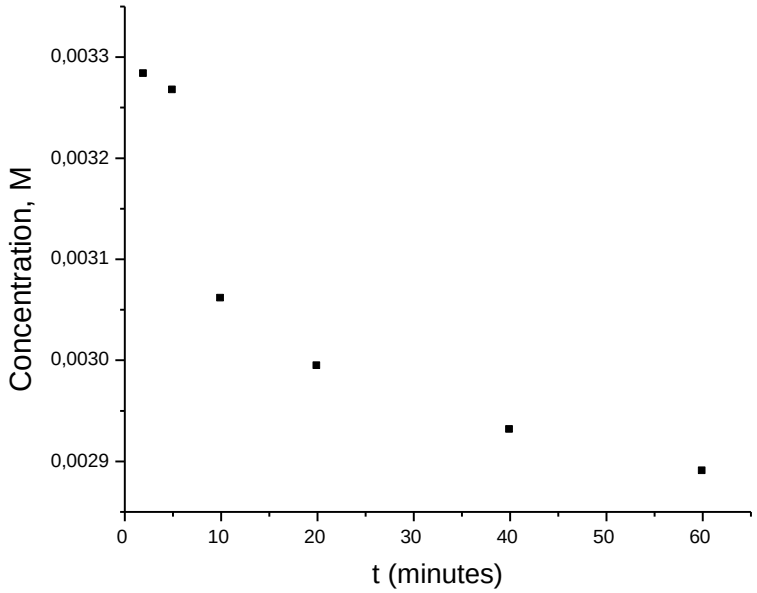

Figure 4.3 : Sorption kinetic of the resin.

Three kinetic models were used to analyze adsorption kinetics which are pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The Lagergren

first-order rate equation **(4.1)** is one of the most widely used equations for the sorption of solute from a liquid solution [47].

$$\log\frac{q_{eq}}{q_{eq}-q_t} = \frac{k_1.t}{2.303} \qquad \textbf{(4.1)}$$

where k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and q_{eq} and q_t show the amounts of adsorption (mg g^{-1}) at equilibrium and at time t, respectively.

The slopes and intercepts of plots of log ($q_{eq} - q_t$) versus t were used to find the pseudo-first-order rate constant k_1 and q_{eq}.

The kinetics of sorption are an important aspect of the process control of removal of pollutants. The linear form of the equation describing the adsorption kinetics by the pseudo-second-order model **(4.2)** is as follows [48];

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}t \qquad \textbf{(4.2)}$$

where q_e is the amount of boron adsorbed at equilibrium (mg g^{-1}); q_t is the amount of boron adsorbed at time t (mg g^{-1}); and k_2 is the equilibrium rate constant of pseudo-second-order sorption (g mg^{-1} min^{-1}).

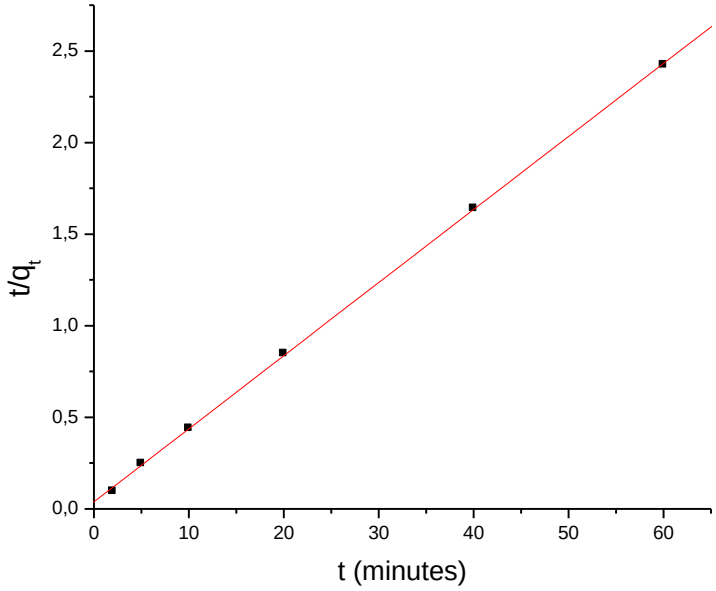

Figure 4.4 : Pseudo-second order model plot for adsorption of boron on the resin.

The rate parameters k_2 and q_e can be found from the intercept and slope of the plot of t/q_t versus t (Figure 4.4). If pseudo-second-order model fits the experimental data, the plot gives a linear relationship which allows to obtain k_2.

The kinetic values obtained by linear regression are reported in Table 4.2. According to experimental and theoretical kinetic data in Table 4.2, the experimental results obtained for the adsorption of boron on resin were found to obey second-order kinetics. In this case, the theoretical q_{eq} value for the resin was very close to the experimental q_{eq} values. In addition, high value of correlation coefficient showed that the data fitted well the kinetic model (Table 4.2).

T**able 4.2** Pseudo-first order and second order kinetic parameters for the adsorption of Boron.

First Order				Second Order		
q_{eq},exp ($mg.g^{-1}$)	k_1 (min^{-1})	q_e ($mg.g^{-1}$)	R^2	k_2 ($g.mg^{-1}.min^{-1}$)	q_e ($mg.g^{-1}$)	R^2
24.756	0.0657	4.83	0.968	0.0413	25.0689	0.999

It may be concluded that adsorption onto boron selective resin consists of chemical interactions due to the fact that the pseudo-second order model suggests that the adsorption process involves the chemisorption mechanism. The chemisorption mechanism is considered to be strong complexation reactions between $B(OH)_4^-$ and diol functions incorporated into the polymeric structure.

Sorption kinetics are controlled by different steps including solute transfer to the sorbent surface, transfer from the sorbent surface to the intra particle active sites and retention on these sites via sorption, complexation and intraparticle precipitation phenomena. Contribution of intra particle diffusion mechanism, can be tested by applying the Weber and Morris equation [49]. In the intraparticle diffusion model the initial rate of intra-particular diffusion is calculated by linearization of the curve **(4.3)**,

$$q_t = K_i . t^{0.5} \quad \textbf{(4.3)}$$

where K_i is the diffusion coefficient in the solid ($mg\ g^{-1}\ min^{-0.5}$).

For intra particle diffusion mechanism, the plot of q_t versus $t^{0.5}$ should be linear Figure 4.5). If the plots are not totally linear, and do not pass through the origin, then intraparticle diffusion could not be the only mechanism involved.

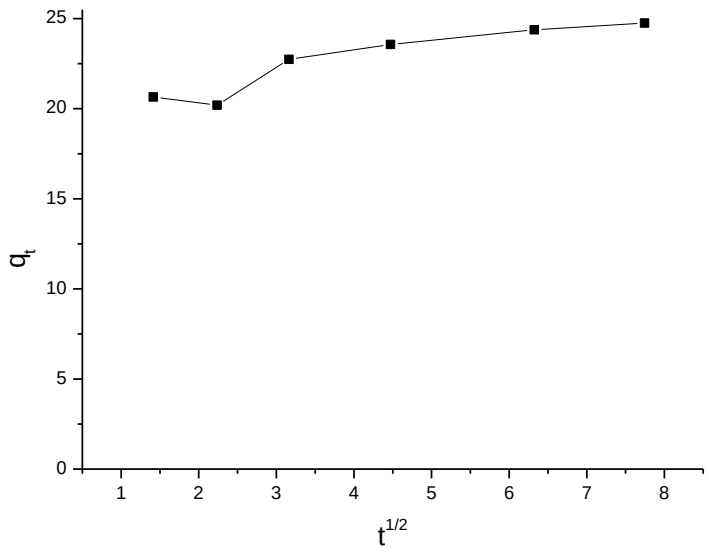

Figure 4.5: Intra-particle diffusion plots for the adsorption of boron on the resin.

The value of intra-particle diffusion rate constant, K_i, are tabulated in Table 4.3. Low K_i and correlation coefficient shows that the intra-particle diffusion rate equation does not fit the adsorption process well.

T**able 4.3** Intra- particle diffusion model for the adsorption of boron.

k_i (mg g^{-1} $min^{-0.5}$)	R^2
1.1853	0.8613

4.3 Regeneration of the Sorbent

Loaded polymer samples, when treated with 2.5 M HCl become almost boron-free. In this way, 2.9 mmol/g boric acid is recovered of loaded sample.

5. CONCLUSIONS

The resin has a potential as an adsorbent for removal of boron from wastewater because it can adsorb boron over a wide pH range.

The desorption capacity of the sorbent was found as 2.9 mmol per gram resin. Desorption experiment was conducted with regenerated resin again and the sorbent was desorbed completely.

The results indicated that polymeric sorbent demonstrates greater potential for the boron removal from aqueous solutions.

REFERENCES

[1] **Chanda, M.** (2000). Advanced polymer chemistry, a problem solving guide. pp. 553-555. Indian Institue of science: Marcel Dekker.

[2] **Ram, A.** (1997). Fundamentals of polymer engineering. pp. 28-30. New York: Plenum Press

[3] **Frechet, J. M. J.** (1994). Functional Polymers and Dendrimers: Reactivity, Molecular Architecture, and Interfacial Energy. *American Society for the Advancement of Science.* Vol. 263(5154), pp. 1710-1715.

[4] **Kim, Y. H. and Webster, O. W.** (1990). Water soluble hyperbranched polyphenylene: "a unimolecular micelle?". *J. Am. Chem. Soc.*. Vol. 112, pp. 4592-4593.

[5] **Malmstrom, E. and Hult, A.** (1997). Hyperbranched Polymers. *Journal of Macromolecular Science, Part C: Polymer Reviews.* Vol. 37(3), pp. 555-579.

[6] **Power, P.P. and Woods, W.G.** (1997). The chemistry of boron and its speciation in plants, *Plant Soil.* Vol. 193, pp. 1–13.

[7] **Murray, F.J.** (1995). A human health risk assessment of boron (boric acid and borax) in drinking water. *Regulatory Toxicology and Pharmacology*, Vol. 22, pp. 221-230.

[8] **Badruk, M., Kabay, N., Demircioglu, M., Mordogan, H., Ipekoglu, U.,** (1999) Removal of boron from wastewater of geothermal power plant by selective ion-exchange resins by I. Batch Sorption-Elution studies. *Separation Science and Technology.* Vol. 34(13), pp. 2553-2569.

[9] **S. Sarp, (**2006). M.S. Thesis, Ege University, Izmir, Turkey.

[10] **Sahin, S.** (2002). A mathematical relationship for the explanation of ion exchange for boron removal. *Desalination*. Vol. 143, pp. 35-43.

[11] **Ross, V. F. and Edwards, J. O.** (1967). The Chemistry of Boron and Its Compounds. In Earl L. Muetterties (Ed), pp. 155-207. New York, Wiley.

[12] **Melnyk, L., Goncharuk, V., Butnyk, I., Tsapiuk, E.** (2005) Boron removal from natural and wastewaters using combined sorption membrane process. *Desalination.* Vol. 185, pp. 147-157.

[13] **Kabay, N., Yilmaz, I., Bryjak, M., Yuksel, M.** (2006). Removal of boron from aqueous solutions by hybrid ion exchange-membrane process. *Desalination*. Vol. 198 pp.158–165.

[14] **Nadav, N.** (1999). Boron removal from sea water reverse osmosis permeate utilizing selective ionexchange resin. *Desalination.* Vol. 124, pp. 131-135.

[15] **Takano, J., Miwa, K., Fujiwara, T.** (2008). Boron transport mechanisms: collaboration of channel and transports. *Trends Plant Sci.*Vol. 13(8), pp. 451-457.

[16] **Kabay, N., Yilmaz, I., Yamac, S., Yuksel, M., Yuksel, U., Yildirim, N.,** Aydogdu, O., Iwanaga, T., Hirowatari, K. (2004). Removal and recovery of boron from geothermal wastewater by selective ion-exchange resins- II. Fieldtests. *Desalination,* Vol. 167, pp. 427-438.

[17] **Brown, P. H. and Hu, H.** (1997) Does boron play only a structural role in the growing tissues of higher plants?. *Plant Soil.* Vol. 196, pp. 211-215.

[18] **Nable, R. O., Banuelos, G. S., Paull, J. G.** (1997). Boron toxicity. *Plant Soi.* Vol. 193, pp. 181-198.

[19] **McLeod, K. W. and Ciravolo, T. G.** (1998). Boron tolerance and potential boron removal by bottomland tree seedlings. *Wetlands.*Vol. 18(3), pp. 431-436.

[20] **Rainey, C. J., Nyquist, L. A., Christensen, R. E., Strong, P. L., Culver, B.,** Coughlin, J. R. (1999). Daily boron intake from the American diet. *J. Am. Diet. Assoc.* Vol. 99(3), pp. 335-340.

[21] **Şimşek, A., Korkmaz, D., Velioğlu, Y. S., Ataman, O. Y.,** (2003). Determination of boron in hazelnut (Corylus avellana L.) varieties by inductively coupled plasma optical emission spectrometry and spectrophotometry. *Food Chem*. Vol. 83, pp. 293–296.

[22] **Melnik, L. A., Butnik, I. A., Goncharuk, V. V.,** (2008). Sorption–membrane removal of boron compounds from natural and wastewaters: ecological and economic aspects. *J. Water Chem. Technol.* Vol. 30(3), pp. 167-179.

[23] **Öztürk, N. and Kavak, D.** (2005). Adsorption of boron from aqueous solutions using fly ash: batch and column studies. *J. Hazard. Mater.* Vol. 127 pp. 81-88.

[24] **Yazicigil, Z. and Oztekin, Y.** (2006). Boron removal by electrodialysis with anion-exchange membranes. *Desalination* Vol. 190, pp. 71-78.

[25] **Yilmaz, I., Kabay, N., Brjyak, M., Yuksel, M., Wolska, J., Koltuniewicz, A.** (2006). A submerged membrane–ion-exchange hybrid process for boron removal. *Desalination*. Vol. 198, pp. 310-315.

[26] **Goncharuk, V. V., Babak, Yu. V., Melnik, L. A., Trachevskii, V. V.** (2011). Removal of boron in the course of pressure-driven demineralization. *J. Water Chem. Technol.* Vol. 33, pp. 307-314.

[27] **Başol, S. and Eren, S.** (1975). "Extraction of BoronByPolyoles", Tübitak Project No. MAG-351, Gaziantep, Turkey.

[28] **Garret, D. E., Week, F. J., Marsh, A. J., Foster, H. R.** (1963). Boron Extractants, U.S. Patent, No: 3111383.

[29] **Grinstead, R. R.** (1972). Removal of Boron and Calcium from Magnesium Chloride Brines by Solvent Extraction. *Industrial Engineering Chemistry Product Research and Development*, Vol. 11, pp. 454-460.

[30] **Yurdakoç, M., Karakaplan, M., Hoşgören, H.** (1999). Effect of Long-Chain Amines on the Extraction of Boron from $CaCl_2$ Brine with CTMP in Petroleum Benzine. *Separation Science and Technology*. Vol. 34(13), pp. 2615-2625.

[31] **Hoşgören, H., Tural, S., Kahraman, F., Tuğrul, M., Karakaplan, M.** (1997). Solvent Extraction of Boron with 1, 2-Dehydroxy-4-Oxadodecane (DHD) in n-Amyl Alcohol. *Solvent Extraction and Ion Exchange*. Vol. 15(2), pp. 249-257.

[32] **Matsumoto, M., Kondo, K., Hirata, M., Kokubu, S., Hano, T., Takada, T.** (1997). Recovery of Boric Acid from Wastewater by Solvent Extraction. *Separation Scienceand Technology*, Vol. 32(5), pp. 983-991.

[33] **Recepoğlu, O. and Beker, U.** (1991). A Preliminary Study on Boron Removal from Kızıldere/Turkey Geothermal WasteWater. *Geothermics*. Vol.20 (1/2), pp. 83-89.

[34] **Simonnat, M. O., Castel, C., Nicolai, M., Rosin, C., Sardin, M., Jauffret, H.** (2000). Boron removal from drinking water with a boron selective resin: is the treatment really selective? *Water Res.* Vol. 34, pp. 109-116.

[35] **Kabay, N., Yilmaz, I., Yamac, S., Samatya, S., Yuksel, M., Yuksel, U., Arda,** M., Saglam, A., Iwanaga, T., Hirowatari, K. (2004). Removal and recovery of boron from geothermal wastewater by selective ion exchange resins. I. Laboratory tests. *React. Funct. Polym.* Vol. 60, pp. 163-170.

[36] **Bicak, N., Bulutcu, N., Senkal, B. F., Gazi, M.** (2001). Modification of crosslinked glycidyl methacrylate-based polymers for boron-specific column extraction, *React. Funct. Polym.* Vol. 47, pp. 175-184.

[37] **Power P.P. and Woods, W.G.** (1997). The chemistry of boron and its speciation in plants. *Plant Soil*. Vol. 193, pp. 1–13.

[38] **Geffen N., Semiat, R., Eisen, M. S., Balazs, Y., Katz, I., Dosoretz, C. G.** (2006). Boron removal from water by complexation to polyol compounds. *J. Membr. Sci.* Vol. 286, pp. 45-51.

[39] **Okay, O., Güçlü, H., Soner, E., Balkaş, T.** (1985). Boron Pollution in the Simav River, Turkey and Various Methods of Boron Removal.

[40] **Simmonot, M., Castel, C., Nicolai, M., Rosin, C., Sardin, M., Jauffret, H.** (2000). Boron Removal from Drinking Water with a Boron Selective Resin: Is the Treatment Really Selective?. *Water Research*, Vol. 34(1), pp. 109-116.

[41] **Bicak, N., Bulutcu, N., Senkal, B. F., Gazi, M.** (2001). Modification of crosslinked glycidyl methacrylate-based polymers for boron-specific column extraction. *Reactive and Functional Polymers*, Vol. 47, pp. 175-184.

[42] **Yavuz, E., Gursel, Y., Senkal, B. F.** (2013). Modification of poly(glycidyl methacrylate) grafted onto crosslinked PVC with iminopropylene glycol group and use for removing boron from water. *Desalination,* Vol. 310, pp. 145-150.

[43] **Sidney, S.** (1967). Quantitative Organic Analysis, (3rd ed). New York: Wiley.

[44] **Basset, J., Denney, R. C., Jeffery, E. H. & Mendham, J.** (1978). Vogel's Textbook of Quantitative Inorganic Chemistry, (4th ed.). pp. 311, London, England: Longman.

[45] **Hatcher, J. T. and Wilcox, L.V.** (1950). Colorimetric determination of boron using carmine. *J. Anal. Chem.* Vol. 22, pp. 567.

[46] **Senkal, B. F. and Bicak, N.** (2003). Polymer supported iminodipropylene glycol functions for removal of boron. *React. Funct.Polym.*, Vol. 55, pp. 27-33.

[47] **Lagergren S,** (1898). Zur theorie der sogenannten adsorption gel ¨ oster

stoffe. *Kungliga Svenska Vetenskapsakademiens Handlingar* Vol.24, pp. 1-39

[48] **Ho Y. S., and McKay G.** (1999). Pseudo-second order model for sorption processes. *Process Biochem.* Vol. 34, pp. 451-465.

[49] **Weber, J., W., J. and Morriss, J., C.,** (1963).Kinetics of adsorption on carbon from solution. *J Sanit Eng Div Am Soc Civil Eng* Vol. 89, pp. 31-60.

CURRICULUM VITAE

Name Surname: Zeynep Ece Erel

Place and Date of Birth: 31.08.1988

E-Mail: zeynepeceerel@gmail.com

B.Sc.: Istanbul Technical University, Chemistry

M.Sc.: Istanbul Technical University, Polymer Science& Technology

PUBLICATIONS/PRESENTATIONS ON THE THESIS

- Poster presentation at EurAsia Waste Management Symposium (2014), Yildiz Technical University (YTU)